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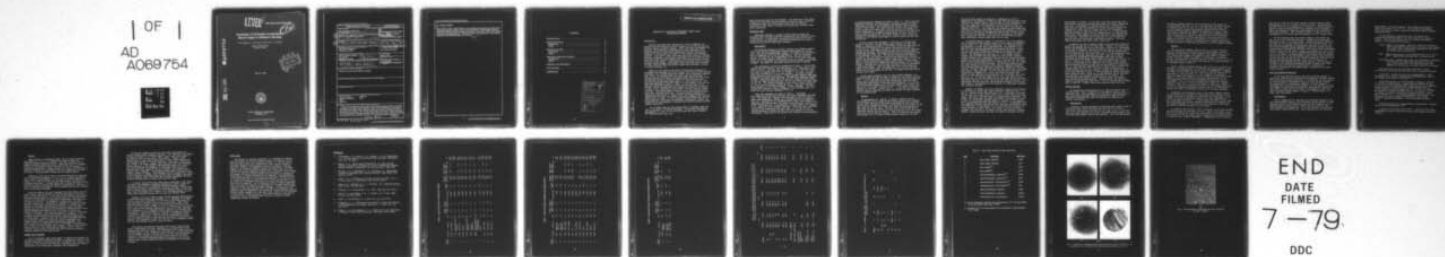
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**Formation of Particulate Contaminants
(Brown Sugar) in Miniature Bearings**

M. K. BERNETT, R. C. BOWERS, H. RAVNER, AND P. J. SNIEGOSKI

*Surface Chemistry Branch
Chemistry Division*

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) There have occasionally been field reports of miniature bearing failures attributed to particulate contaminants which, because of their appearance under low-power magnification, have been given the descriptive term "brown sugar". This study examines the formation of particulates under both dynamic and static conditions. The lubricants include diesters, polyol esters, a silicone, and mineral oil; the bearing surfaces or substrates were 52100 steel, 440C steel, and Pyrex. Particulate formation was readily achieved under boundary lubrication. The resultant films adhered tenaciously and 254 950 (Continues)		

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20. Abstract (Continued)

resisted rinsing or wiping. Surface analysis by X-ray photoelectron spectroscopy and Auger electron spectroscopy indicated the presence of iron oxides and probably iron-organics (soap) compounds. Under static conditions exposure of thin films of lubricants to light or heat (100°C) did not generate lubricant-derived particulate products. This exposure did have one adverse effect, viz. the complete depletion of several antioxidants after only a few hours.

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FORMATION OF PARTICULATE CONTAMINANTS (BROWN SUGAR)
IN MINIATURE BEARINGS

INTRODUCTION

Precision miniature ball bearings are critical components of guidance and other sensitive control systems for civilian and military aircraft, ships, and space vehicles. Where low-torque requirements are mandated, the acquisition or generation in these bearings of even minute quantities of particulate contaminants can have serious consequences to the operation and safety of the vehicles and personnel involved. From time to time, there have been field reports of bearing failures attributed to particulate contaminants which, because of their appearance under low-power magnification, have been given the descriptive term "brown sugar". Such deposits have even been noted on unused bearings during storage, particularly those lubricated with silicones. In these cases the white particulates formed were presumably a result of polymer formation (1).

Baxter (2) has reported two cases of brown sugar formation in instrument ball bearings; the first occurred with a 440 C steel bearing lubricated with a Specification MIL-L-6085A, bis(2-ethylhexyl) sebacate base, fluid. He concluded that the brown sugar was essentially a reaction product of the ester and bearing metal within the wear track. The sequence probably involved formation of the half-ester which reacted with the activated metal surface to form a metal soap. The soap then hydrolyzed to the M^{++} oxide. In this example it was not the lubricant which was oxidized but rather the surface layer of the bearing. Baxter reported that this problem was empirically resolved by using an oil conforming to MIL-L-23699, a polyol ester jet engine lubricant. The second example involved a 440 C steel bearing lubricated with a perfluoroether oil. The brown deposit observed in this bearing was described as a "brittle glass" containing significant quantities of iron and iron oxides; the glassy component had a melting range of 200° to 230°C. In this instance it was deduced that the oil had polymerized, resulting in catastrophic bearing wear. Baxter concluded that in both examples "a wearing steel surface exhibits extreme chemical reactivity".

It is evident that the term "brown sugar" is somewhat vague and that it can apply to different phenomena. The present investigation was initiated to study the factors affecting brown sugar formation

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under controlled laboratory environments. Two sections of this report consider the lubricant and metal-surface interaction under conditions of mechanical wear; the third section deals with the chemical reactivity of thin films of lubricant on bearing metal surfaces under static conditions.

MECHANICAL WEAR

Experiments designed to simulate metal-to-metal contact and mechanical wear take many forms and concomitantly give different types of information. A pin-on-disk type apparatus was selected for the present study with experimental conditions deliberately set severe to accelerate wear and/or brown sugar formation.

Experimental

The apparatus employed as sliders one-half inch diameter spheres rather than the more conventional hemispherically-ended or conical pins. The slider was dead-weight loaded. The normal force was one kg and the temperature 23°C for all experiments. Both the rotational speed of the disk and the circumference of the circular path were varied; the linear velocity ranged from 0.37 to 3.1 cm sec⁻¹, although during any one experiment the rotational speed and linear velocity were constant. The number of revolutions varied from 1900 to 180,000.

The experimental results are summarized in Table 1. Pin and disk combinations were always of the same material (i.e. 52100 steel, 440 C steel or Pyrex). The disks used in experiments No. 1 through 19 were two inches in diameter and in No. 20 through 25, 3/4 inch. All steel disks were polished with 0.3 µm alpha alumina. The highly polished Pyrex disks were used as received. Vickers hardness numbers (VHN) were determined for one of each type disk. The VHN (and equivalent Rockwell C) were: large 52100 steel disk, 650 (Rc 58); large 440C steel disk, 750 (Rc 62); small 52100 steel disk, 595 (Rc 57); small 440C steel disk, 735 (Rc 62). The reported hardness of both types of steel sliders was Rc 58 to 64 and the surface finish was one µm. The Pyrex disk had a Knoop Hardness of 470 (Knoop Hardness = Vickers Hardness). The Pyrex sliders were reported to have a hardness of 6 on the Mohs Scale (ca. Knoop 550) and a surface roughness of 5-10 µm.

Wear test parameters are given in Table 1. Lubricants MIL-L-6085A and MB 20B (MIL-L-818-46) were fully compounded instrument oils. The former was a sebacate diester-based oil and the latter a mixed bis(2-ethylhexyl) azelate and a pentaerythritol tetracaproate-base (3). Lubricant HC is a pentaerythritol ester; MIL-L-23699B is a compounded gas turbine engine oil based on the same type of ester as HC fluid. The mineral oil, a non-additive colorless liquid, was selected as an example of a poor boundary lubricant. Additives used to minimize rusting in the experiments with water (Nos. 12, 13, and 24) were sodium phosphate and sodium nitrite; both were present in 0.5% concentrations. Wear scars on the sliders were obtained from measurements

on photomicrographs; examples are shown in (Fig. 1). These scars were sometimes elliptical and occasionally irregularly shaped; the dimensions given in Table 1 are the maximum and minimum, usually perpendicular to each other. The track width on the disk also varied from point to point on a single track; the value given is an average of several measurements. A series of profiles was made on the wear track with a Talysurf 4 profilometer; maximum depths for each trace were averaged and recorded in μm . The final column in Table 1 gives the variation in the kinetic coefficient of friction during the last few revolutions.

In each pin-on-disk experiment, a few drops of lubricant were applied to the disk. As the slider passed through the drops they tended to coalesce and adhere to the slider, having the same effect as if the drop of lubricant in the contact region moved around the circular track. Wear debris formed in the contact area was dispersed through the lubricant drop and precipitated onto the disk forming a band around the track. The width of this film was approximately equal to the diameter of the drop. The film was tenacious and remained attached to the disk after the lubricant was removed with isopropyl alcohol and acetone solvents. Figure 2 shows what appears to be a network of finely divided wear particles (light areas) or brown sugar. Before the lubricant was removed the film was usually, but not always, evident. The wear scar on the slider was nearly always surrounded by a dark brown deposit. Since the same small area on the slider was always in the contact zone, the deposit was on it was more concentrated than was the deposit on the disk. No deposit was found within the wear scar itself.

In all roller bearings, there is some sliding component, e.g. slipping between the ball and race or sliding of the retainer and race land. It is at the areas of sliding contact that wear most generally occurs, and as indicated earlier the experimental conditions were deliberately made severe to accelerate wear formation. At a one-kg load the Hertzian pressure for a 1/2-inch diameter steel slider on a steel flat is 58 kg mm^{-2} (82,000 lbs in^{-2}). For Pyrex on Pyrex this pressure is 12 kg mm^{-2} (17,000 lbs in^{-2}). At the areas of intimate asperity contact, pressures can equal the Vickers (or Knoop) Hardness of the sliding solids.

Results

In experiments No. 1 and No. 2 (Table 1) results with the MIL-L-6085A oil and its sebacate base without additives are compared. In both cases the area on the slider surrounding the wear scars was covered with a dark-brown deposit, the lubricant in the vicinity of the wear track was cloudy, and a thin solid brown film was deposited on both sides of the wear track. The wear scar on the slider was unexpectedly smaller and the number of wear particles in the fluid were fewer with the non-additive diester. After the lubricant was removed with solvent (No. 2) a film of brown material adhered to the disk.

The film neither melted nor softened at temperatures to 225°C, suggesting it was neither a polymer nor wear particles attached to the surface by an organic binder. After cooling to room temperature, the disk was a deep blue (the interference color produced by Fe_3O_4 or Fe_2O_3 approximately 0.1 μm thick) but the wear track was still the original steel color. This indicates the presence of some undetected continuous film on the track which prevented the formation of an oxide layer, and an evident but discontinuous deposit near the wear track. The disk was then reheated to 300°C with no softening of the deposit. After cooling the disk was a pale blue and the track straw yellow, again indicating a thinner oxide layer on the track.

As detailed earlier, Baxter (2) proposed in one of his examples that a metal-half ester reaction product (a metal soap) hydrolized to a metal oxide, i.e. the observed brown sugar. To determine whether the presence of a metal was a requirement for the formation of an adherent film, the wear experiment was repeated with Pyrex on Pyrex (No. 17), with bis(2-ethylhexyl) sebacate as the lubricant. After 180,000 revolutions no wear could be detected on either the disk or slider. The conditions for this test, i.e., the highest sliding velocity and the lowest Hertzian pressure, were the most likely to promote formation of a continuous fluid film at the sliding interface, probably in the elastohydrodynamic region. When the test was rerun using a low-viscosity mineral oil at a slower velocity (No. 18), heavy wear occurred after 50,000 traverses. The lubricant appeared clear, but after rinsing with acetone a white deposit remained (presumably fine powdered glass wear particles) tenaciously adhering to the disk surface. The wear track was wide and deep and, unlike any of the other wear tracks, highly polished. If the cross section of the groove is considered as a segment of a circle, the volume calculated from product of this area and the circumference of the circular wear track was $4.7 \times 10^{-4} \text{ cm}^3$ and the weight loss 1.1 mg. With water as the lubricant (No. 19) the wear groove on the Pyrex disk was not polished. The volume loss was $17.1 \times 10^{-4} \text{ cm}^3$ after only 2800 revolutions. It is significant that the fine wear debris adhered strongly to the surface even though it was generated in the absence of a hydrocarbon lubricant and a metallic surface.

Mineral oil, MB20B, and bis(2-ethylhexyl) sebacate were evaluated as lubricants for 52100 steel under comparable conditions (Nos. 3, 4, and 5). Similar results were obtained, i.e., a light-brown area near the wear scar and a thin, brown, solid film on both sides of the wear track. The size of the wear scars on the slider were comparable. The greater wear track width and depth with MB20B is attributed, at least in part, to the smaller hardness number of the disk, ca 500 Vickers, due to its having previously been heated to 300°C. In experiment No. 6 with dimethyl silicone, friction and wear were both exceptionally high for 52100 steel, in accordance with the well-known poor boundary condition behavior of these fluids. The deposit on the disk adhered strongly, but relative to the amount of wear there was only a modest deposit, unlike the usual case where the amount of adherent film was

proportional to the wear. In the case of the more severe wear with the silicone, the wear particles were perhaps too large to adhere and were lost. To determine if a monomolecular layer of stearic acid would adsorb in the area adjacent to the wear track and prevent the formation of a film, one % of stearic acid in bis(2-ethylhexyl) sebacate was used to lubricate 52100 steel (No. 7). A heavy deposit, which was unusually light in color, remained after the lubricant was rinsed away. This deposit was readily removed by light rubbing with a cotton swab. With water as the lubricant (No. 8), friction was high and wear very severe after relatively few passes. The heavy, light-brown deposit was rather easily rubbed away.

In general the type of deposit formed on the 440C steel disks and sliders was the same as on the 52100 steel. However, the quantity of deposit was markedly less on the 440C steel, probably as a consequence of its greater hardness. When MIL-L-6085A oil was run for only 10,000 revolutions, no solid film was visible on the disk but a small dark area was detected near the slider wear scar. At room temperature under the stringent sliding conditions used here, there was no obvious difference in the amount of deposit between 440C steel surfaces lubricated with MIL-L-6085A, MIL-L-23699B, and mineral oil (Nos. 9, 14, and 11). Baxter (see above) found that brown sugar formed on 440C steel in the presence of MIL-L-6085A oil but not with MIL-L-23699B. Heavier deposits occurred on 440C with the non-additive HC base stock (No. 16) than with the compounded MIL-L-23699B oil which contains the antiwear agent, TCP (No. 15). With water (which contained rust inhibiting additives) as the lubricant, sliding was characterized by severe wear and high friction. It was necessary to replace evaporated water during the test. After the run was completed and all the water had evaporated, the additives crystallized on the surface. The crystals were easily washed off with distilled water uncovering a heavy dark-brown tenacious deposit. Reproducibility was tested by repeated experiments with water (Nos. 12 and 13) and with MIL-L-23699B (Nos. 14 and 15). Similar results were obtained within each set.

SURFACE ANALYSIS

The mechanical processes employed to create and measure wear, as described above, gave no insight as to the chemical nature of the deposited films. This information was obtained on films deposited on wear tracks employing Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) for analysis of elemental and chemical constituency.

Experimental

A series of sliding experiments was designed with smaller disks of 52100 steel (Nos. 20-23) and 440C steel (Nos. 24-25) in Table 1 suitable for spectroscopic analysis of the films in situ. On any one wear track area (selected for visually observable heavy deposit), the following spectroscopic approach was employed: (a) A full XPS spectrum

to observe elemental species; (b) high resolution XPS spectra for selected peaks, such as O, C, Fe, S, and any other identified element of interest, such as Ba; and, (c) a full AES spectrum, taken last to avoid possible electron beam damage affecting the XPS results. Data on these experimental samples were compared to similar spectra from several reference specimens: a freshly glow-discharged 440C steel to ascertain the surface constitution of the clean substrate steel; a chlorinated silicone deposited on 440C steel, where the amount and chemical nature of each element in the deposit were well defined; and on two samples of powdered ferric stearate (pressed into an indium backing) to establish the spectra of an iron organic compound.

Results

The significant elements observed were C, O, and Fe (Table 2); XPS line intensities and line positions (binding energy) of these elements are indicative of their abundance and chemical nature, e.g., the O traces might suggest the presence of iron oxide or carboxyl groups, and the C traces the presence of hydrocarbon, ubiquitous air-born contamination, or carboxyl groups. Traces of S, Cl, N, Ba, Cu, Na (the last on No. 24 only) were also observed on various specimens in different amounts (Table 3).

Table 2 shows the binding energies (BE) in eV of C, O, and Fe, as obtained in the XPS spectra. All C signals were predominantly in the BE range of approximately 285 eV which is the assignment for aliphatic C-C bonds (4), but peaks were also observed in the BE range of 289 eV indicative of carboxyl groups (5). The C signals also included traces of other C-O linkages too poorly defined for consideration here. Peaks of the O signal occurred at energies characteristic of the following bonds: a BE of 530.5 eV indicated an oxide (6) such as iron oxide; a BE of \sim 531.5 eV indicates Si-O bonds (see reference surfaces), and a BE of \sim 532.5 eV indicated C-O bonds (7). The Fe signals of \sim 711.6 eV indicated iron oxide (8); the somewhat higher BE of 712.8 eV suggested a different chemical state of Fe, possibly an organic salt such as determined from the ferric stearate reference.

Approximate stoichiometric ratios of the major elements present in the surface can be obtained by correcting the XPS intensity of the element according to its specific sensitivity and normalizing it with respect to one of the elements. Ratios for C and O normalized to Fe = 1 are shown in Table 2. A C ratio larger than that for the clean glow-discharged steel surface probably originated from a deposit, and the relative abundance of that ratio thus is a measure of the thickness and/or molecular structure of that deposit.

It should be noted, however, that an overlayer on the metal specimen effectively masks the electrons of the Fe. Thus, as the signal intensity of C increases (be it from oil, contamination, or surface product), the intensity of the Fe signal, whether originating from wear particles or from the steel surface, decreases. A comparison of the C-C ratios

with the C-O ratios in the ferric stearate reference samples yields approximately 21 to 22 C-C bonds for each C-O bond. This proportion is close to the 17 C-C linkages per C-O linkage in a stearate molecule. However, since the purity of the ferric stearate was not precisely known, the presence of additional constituents may have contributed to the larger proportion. The Fe signals indicate a ratio of one Fe to approximately 3.5 C-O bonds which corresponds to a Fe^{+3} valence state.

The data indicate that the deposit created by the mineral oil (No. 22) is fairly light and that the O is mainly in the iron oxide state with traces of C-O bonds present. Deposits from MIL-L-6085A oil, on 52100 (No. 20) and 440C steels (No. 25), and from MB-20B (No. 21a) have high carbon contents (as evidenced by the large C-C ratio), and the C-O and O signals suggest substantial amounts of carboxyl groups. A second area on specimen 21b (MB-20B), with a less visually discernible deposit, showed not only lower C content, as expected, but also a lower C-O to C-C ratio; the O and Fe binding energies here were more indicative of iron oxide. The oxygen signal of the deposit from the dimethyl silicone oil (No. 23) had two definite peaks of almost equal intensity, one for the oxide and one for the siloxane linkage (as observed in the reference silicone-coated specimen) and a low C-C intensity, in keeping with the comparatively low carbon content of the silicone oil. The water - rust inhibitor formulation showed C signals unduly high to arise solely from the small percentage of rust inhibitor; additional contamination of unknown origin is suggested as an additional C source.

THIN FILM LUBRICANT STABILITY

It has been indicated earlier that there have been reports of particulate formation in stored lubricated instrument bearings, particularly those with silicone lubricants. At present the use of silicones in these bearings is discouraged, except for very special purposes. The susceptibility to particulate formation of other classes of instrument oils, particularly ester-based, is of considerable interest. This segment of the study was initiated to determine the stability of thin films of these oils in the types of environments to which they might be exposed during assembly, storage, or transportation, i.e., light, heat and humidity.

Experimental

Table 4 summarizes the lubricants and substrates employed in the thin film stability studies. The lubricants included several of those described earlier in the mechanical wear section in addition to two pentaerythritol valerate esters. Before use, the 52100 and 440C steel platens were polished with 0.3 μm alpha alumina; all substrates were solvent cleaned before use. Small quantities of the lubricants

were spread on the platen surfaces, the average film thickness being of the order of 5×10^{-4} cm. This thickness approximated that calculated for several operational miniature bearings examined during this study.

The environmental conditions to which the samples were exposed were generally harsher than those normally encountered in service. This was deliberately done to accelerate any adverse effects. The conditions selected were:

Light - Samples were exposed to 800 foot candles of fluorescent light by positioning the platens 15 cm from a lamp holding two 15-watt tubes. Exposure was continued for one week and samples were observed daily.

Heat - Samples were stored at room temperature and in an oven at 100°C . Observations were made over a two-week period.

Acid-water vapor - Samples were stored in a desiccator containing a 50-50 mixture of concentrated hydrochloric acid and water in the lower well. The metal substrates were exposed for one week and the quartz plates for two weeks.

The reactions of the oils and their additives to these environmental conditions were monitored by the following procedures:

Octyl-PANA: Analyzed by thin layer chromatography. After development of the plates, densitometry measurements were made of the colored spots formed on standing (9).

Hydrolysis products of bis(2-ethylhexyl) sebacate: Analyzed by gas liquid chromatography. Separations were carried out with a 6 ft by 0.125 inch stainless steel column packed with a commercial packing material 3 percent SE-30 on 100/120 mesh Gas Chrom Q. Column temperature was programmed from 150° to 264°C in 8 minutes. The helium flow through the column was 20 cc per minute. To the oil samples was added a commercial silylation material, Trisil, Pierce Chemical Co., to form chromatographable derivatives of any half-ester or diacid produced by hydrolysis of the diester. Authentic samples were prepared to obtain reference retention data.

Hydrolysis products of pentaerythritol tetravalerate: Analyzed by gas liquid chromatography (10).

2,6-Di-tert-butyl-para-cresol (DTBC): Analyzed by gas liquid chromatography under the same conditions as the sebacate hydrolysis products.

Results

Under exposure to fluorescent light, the oil films containing octyl-PANA, A, B, E, F, G, H, assumed an orange hue while the remaining samples remained colorless. This color formation in the samples containing octyl-PANA was not unexpected since it represents oxidation of the additive and is the basis of the TLC method of analysis described here. Light exposure of 16 hours was sufficient to completely deplete the octyl-PANA in the above samples and the DTBC in C and D. No particulates formed from the exposed samples.

Exposure to 100°C in an oven for 16 hours resulted in a decrease of the octyl-PANA in samples A, B, E, F, G, H, to about one-third of their original concentrations. In the case of the MIL-L-6085A oil, samples C, D, after only two hours the DTBC additive was depleted to an undetectable level. It seems likely that a large proportion of this relatively volatile additive was removed by evaporation. After two weeks of heating, the volumes of the oil samples were greatly decreased but no particulates developed.

Since the subject oils are formulated from both dibasic acid and polyol esters, they are capable of reacting with water to form the parent acids and alcohols. In the case of the sebacates and azelates, the parent diacids have very low solubilities as do the polyol component of the valerates; if generated by hydrolysis, they would precipitate from the oil. The presence of strong acid in the tests described would tend to accelerate any tendency to hydrolysis; nevertheless, no hydrolysis products were detected. In several days of exposure to the vapors of hydrochloric acid and water, the metal platens used with the additive and nonadditive containing oils C and I corroded beneath the surface of the oil as well as on the bare surface of the metal. The corrosion inhibitor in sample C was unable to impart protection under these extremely acid conditions. The corrosion products were brown and gritty, possible characteristics of "brown sugar". However, since the corrosive environment here was unrealistically severe, the corrosion products generated would probably never occur under normal operational conditions. The particulates were not analyzed, but it is reasonable to assume they were a mixture of metal oxides and chlorides. Since no acid products formed from oils on the quartz plates, samples J and K, there is therefore little reason to believe that metal soaps were present as component deposits on the metal plates.

SUMMARY AND DISCUSSION

Use of the generic term "brown sugar" to identify particulate contaminants in precision miniature bearings is unfortunate, insofar as no precise description of the material has, or probably can be given. The laboratory study reported here employed a mechanical wear and chemical degradation of the lubricants to generate such contaminants.

Particulate formation during the pin-on-disk experiments was readily achieved under boundary conditions. The results did not conform to Baxter's example (2) of "brown sugar" being a very high polymer of the lubricant (in that instance a fluorocarbon). Baxter's other example was of "brown sugar" identified as a metal oxide generated by the following sequence — diester lubricant + half ester + metal soap + metal oxide. Our results suggest some correlation with that mechanism. Surface analysis of the residual film deposited around the circular wear track indicates the presence of iron-oxides (wear particles), adsorbed ester (not removed by solvent cleaning), and possibly iron-organic (soap) compounds. The deposited films adhered tenaciously and resisted rinsing or wiping. This adherence was not necessarily a result of the reaction of activated metal surfaces with the organic lubricants, since an adherent white film, which had a similar appearance, was also formed by sliding Pyrex on Pyrex lubricated with water.

To date it would appear that under static conditions of the liquid lubricant films examined, reasonable temperatures (100°C), light and acid-water vapor do not by themselves generate lubricant-derived particulate products on bearing metal or quartz surfaces. Particulates that do develop under liquid films on 52100 bearing steels in the acid-water vapor environment do not appear to be lubricant-related, but are likely metal reaction products such as oxide and chloride salts.

Exposure of the oil films to light and heat affected them adversely in ways other than particulate formation, i.e., depletion of the additives by two routes, evaporation in the case of the widely-used DTBC, and (presumable) oxidation in the case of octyl-PANA. These raise important questions which cannot be satisfactorily answered at this point. The first refers to DTBC; if it is so rapidly lost from the thin film system at even moderate temperatures, why are the many instrument oils containing it as a component additive effective in bearings over long periods? The second refers to octyl-PANA; although its depletion is probably a result of an oxidative process, the mechanism of this process is not understood. There is some very preliminary evidence that the depletion cannot be explained as due simply to reaction of the additive with atmospheric oxygen; the identity of the oxidation products and their antioxidant activity is also not known.

The chemical and physical processes which lead to particulates and/or "brown sugar" will vary, depending on the composition of the bearing metal-lubricant system, the environment (heat, light, access to oxidizing agents, trace contaminants and catalysts), and operating mode. It would appear, however, from our studies to date that wear-induced effects on the bearings and lubricants, rather than the intrinsic stability of properly formulated qualified instrument oils, are the primary cause of particulate/brown sugar contamination in instrument bearings.

FUTURE WORK

The efficacy of oxidation inhibitors is a fundamental parameter which determines not only how thermally stable the lubricant is, but also the useful life of the associated bearing. In thin oil films, inhibitors assume even more significance, since they are present in such small amounts. The mechanism by which octyl-PANA is depleted appears to be primarily oxidative rather than evaporative. An understanding both of the depletion mechanism and of the constitution and role of the inhibitor oxidation products will contribute to the ultimate development of more efficient additive and instrument oil systems; an investigation of these processes will be commenced. The consequences of the rapid depletion of 2,6 ditertbutyl-para-cresol (DTBC) from thin oil films should also be investigated both because of the wide use of the additive in instrument oils, and the critical applications in which these oils are employed. The investigation should include a determination of the additive contents of lubricants from recently manufactured, long-term stored, and used instrument bearings. A study of the surface chemistry of operating bearings whose lubricants are depleted of the additive should be undertaken; the results may indicate whether additive-induced surface changes, e.g., adsorbed films, account for or contribute to the efficacy of the lubricants. This study should be conducted in conjunction with an appropriate NARF facility to conduct relevant engineering studies as required.

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Table 1: Wear and Friction Conditions and Results

Experi- ment No.	Pin-Disk	Lubricant	RPM	Circum- ference (cm)	Linear Velocity ₁ (cm-sec)	Revolutions	Distance (km)	Diameter of Wear Scar (mm)	Track Width (mm)	Maximum Track Depth (μm)	μk
1	52100	MIL-L-6085A	30	6.3	3.1	153,000	9.6	0.66 0.69	0.66	0.70	0.095 0.15
2	52100	Bis(2-ethylhexyl) Sebacate	30	6.3	3.1	180,000	11.3	0.39 0.52			0.095 0.115
3	52100	Mineral Oil	18.3	6.3	1.9	50,000	3.2	0.48 0.48	0.37	0.15	0.02 0.08
4	52100	MB-20B	18	6.3	1.9	50,000	3.1	0.43 0.45	0.45	1.3	0.125 0.15
5	52100	Bis(2-ethylhexyl) Sebacate	18	6.3	1.9	50,000	3.1	0.39 0.44	0.30	0.36	0.07 0.12
6	52100	Silicone (Dimethyl)	19	7.2	2.3	30,000	2.2	0.71 0.75	0.86	1.3	0.11 0.26
7	52100	Bis(2-ethylhexyl) Sebacate plus 1% stearic acid	19.8	6.9	2.3	30,000	2.1	0.43 0.44	0.48	0.2	0.11 0.13
8		Water	18	6.3	1.9	1,900	0.12	1.04 1.10	1.07		0.35 0.41
9	440C	MIL-L-6085A	18.3	6.3	1.9	50,000	3.2	0.34 0.38	0.30	0.81	0.115 0.135
10	440C	MIL-L-6085A	3.5	6.3	0.37	10,000	0.6	0.26 0.27	0.19	0.44	0.13 0.135
11	440C	Mineral Oil	18	6.3	1.9	50,000	3.1	0.22 0.23	0.22		0.09 0.10

Table 1: Wear and Friction Conditions and Results (Cont'd)

Experi- ment No.	Pin-Disk	Lubricant	RPM	Circum- ference (cm)	Linear Velocity (cm-sec ⁻¹)	Revolutions	Distance (km)	Diameter of Wear Scar (mm)	Track Width (mm)	Maximum Track Depth (μm)	μk
12	440C	Water Plus Additives	18.5	5.0	1.6	2,400	0.12	1.02 1.02			0.38 0.44
13	440C	Water Plus Additives	19.4	5.7	1.9	2,500	0.14	1.03 1.05			0.22 0.40
14	440C	MIL-L-23699B	20	6.9	2.3	29,000	2.0	0.32 0.37	0.23	0.55	0.09 0.115
15	440C	MIL-L-23699B	20.5	6.9	2.4	30,000	2.1	0.42 0.42	0.29	0.70	0.09 0.115
16	440C	HC	19.4	6.6	2.1	30,000	2.0	0.37 0.39	0.88	1.1	0.11 0.12
17	Pyrex	MIL-L-6085A	30	6.3	3.1	180,000	11.3				0.075 0.095
18	Pyrex	Mineral Oil	18.3	6.3	1.9	50,000	3.2	1.02 1.20	1.5	7.8	0.05 0.15
19	Pyrex	Water	18	6.3	1.9	2,800	0.18	2.8 3.0	3.4	12	0.35 0.55
20	52100	MIL-L-6085A	19.8	3.8	1.2	30,000	1.1	0.50 0.50	0.31	0.23	0.09 0.11
21	52100	MB-20B	19.8	3.8	1.2	30,000	1.1	0.36 0.37	0.43	0.5	0.115 0.135
22	52100	Mineral Oil	19.8	3.8	1.2	30,000	1.1	0.44 0.45	0.28		0.085 0.105

Table 1: Wear and Friction Conditions and Results (Cont'd)

Experi- ment No.	Pin-Disk	Lubricant	RPM	Circum- ference (cm)	Linear Velocity (cm-sec)	Revolutions	Distance (km)	Diameter of Wear Scar (mm)	Track Width (mm)	Maximum Track Depth (μ m)	μ k
23	52100	Silicone (Dimethyl)	18.7	3.6	1.1	28,000	1.0	0.68 0.74	1.1		0.11 0.23
24	440C	Water Plus Additives	18.5	5.0	1.6	2,400	0.12	1.35 1.39			0.17 0.46
25	440C	MTL-L-6085A	19.8	3.8	1.2	30,000	1.1	0.55 0.56	0.32		0.09 0.13

Table 2: Binding Energies and Relative Ratios of C, O and Fe on Steel Surfaces as Determined by XPS (Normalized to Fe = 1)

Sample	C-C			C-O			O			Fe		
	BE(ev)	Ratio		BE(ev)	Ratio		BE(ev)	Ratio		BE(ev)	Ratio	
20	285.8	46.1		289.3	7.7		532.8	15.9		712.8	1	
21 (a)	285.4	37.8		289.6	5.6		532.1	12.6		712.8	1	
(b)	285.4	12.3		289.3	1.1		530.7	6.1		711.7	1	
22	285.2	7.8		289.3	1.0		530.4	6.3		711.5	1	
23	285.4	9.8		289.3	0.9		531.8	8.2		711.6	1	
							530.3	7.5				
24	285.4	34.1		289.3	5.5		531.8	15.7		712.0	1	
25	285.8	53.1		289.2	9.3		532.4	18.3		712.6	1	
Reference Samples												
440C (Glow Dis)	284.9	1.3		-	-		530.6	7.5		711.8	1	
Chlorinated Silicone on 440C	284.1	360		-	-		531.7	176.0		711.8	1	
Ferric Stearate (1)	285.0	115.7		289.3	5.3		532.1	12.8		712.6	1	
Ferric Stearate (2)	285.0	121.9		289.2	5.6		532.0	11.6		712.7	1	

Table 3: Elements Other Than C, O, and Fe on Steel Surfaces as Determined by XPS and AES

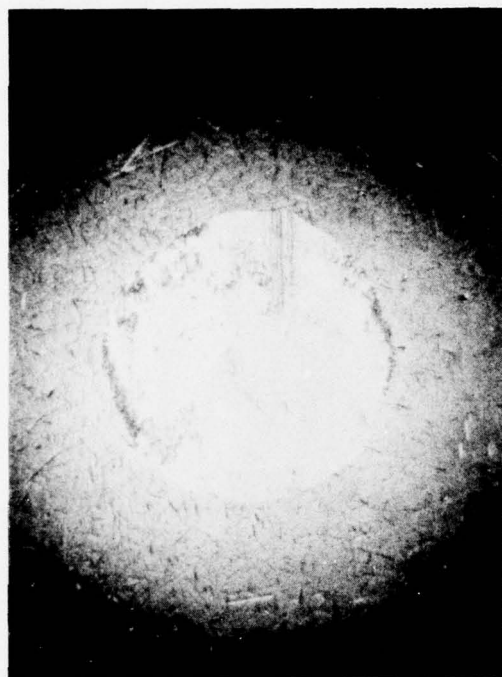
Sample	S	Cl	N	Ba	Cu	Na	Si
20	X	Trace		X	Trace		
21 (a)	X	X		X	Trace		
(b)	X	X		X	X		
22	X	X			X		
23	Trace	Trace					X
24	X	X	X			X	
25	X	X		X			

Table 4: Thin Film Lubricant Study Conditions

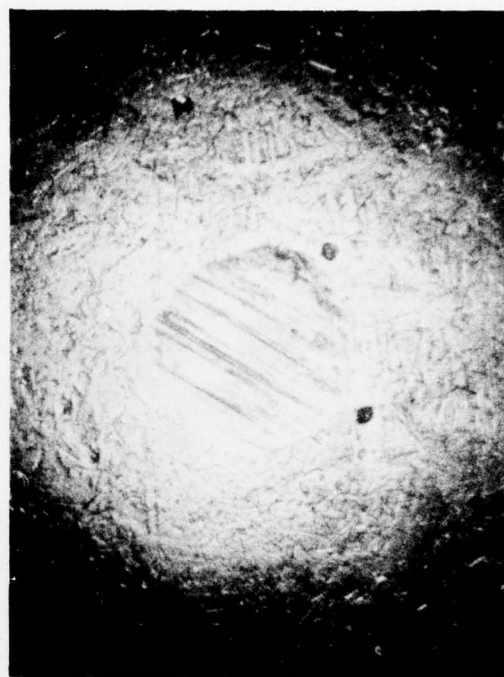
<u>Code</u>	<u>Lubricant</u>	<u>Substrate</u>
A	MIL-L-81846 (MB-20B)	52100
B	MIL-L-81846 (MB-20B)	440C
C	MIL-L-6085A ⁽¹⁾	52100
D	MIL-L-6085A ⁽¹⁾	440C
E	Bis(2-ethylhexyl) sebacate ⁽²⁾	52100
F	Bis(2-ethylhexyl) sebacate ⁽²⁾	440C
G	Pentaerythritol tetravalerate ⁽²⁾	52100
H	Pentaerythritol tetravalerate ⁽²⁾	440C
I	Bis(2-ethylhexyl) sebacate	52100
J	Bis(2-ethylhexyl) sebacate	Quartz
K	Pentaerythritol tetravalerate	Quartz

(1) Bis(2-ethylhexyl) sebacate base containing 1% of the antioxidant 2,6-di-tertbutyl-para-cresol (DTBC)

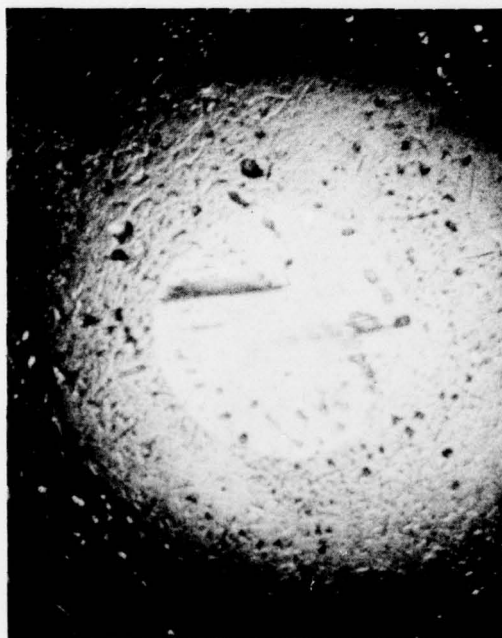
(2) Contains 1% of the antioxidant N-p-octylphenyl- α -naphtaylamine (octyl PANA)



(a)



(b)



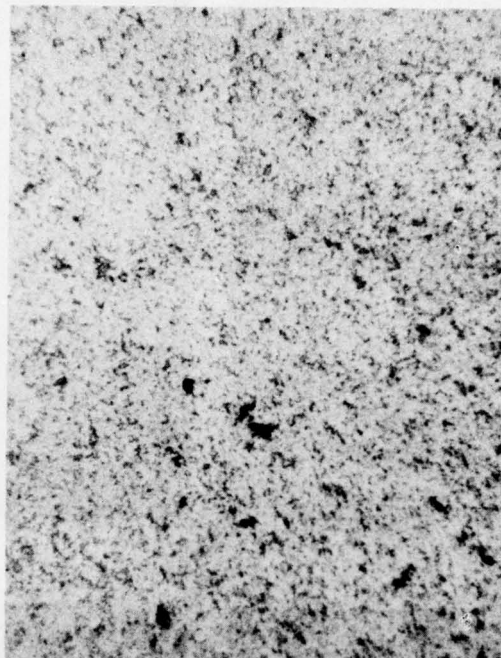
(c)



(d)

0.1mm

Fig. 1 — Wear Scars on 52100 Steel Sliders Lubricated with (a) MIL-L-6085A, No. 20, (b) MB20, No. 21, (c) Mineral Oil, No. 22, and (d) Dimethyl Silicone, No. 23.



10 μ m

Fig. 2 — Film Deposited on 52100 Steel Disk After Lubrication
with MIL-L-60858.